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**UNIVERSITY OF TORONTO
STUDIES**

**PAPERS FROM THE CHEMICAL
LABORATORIES**

No. 51: THE DETERMINATION OF PHENOL, BY S. J. LLOYD

**No. 52: TRIBROMPHENOLBROMIDE, ITS DETECTION,
ESTIMATION, RATE OF FORMATION, AND REACTION
WITH HYDRIODIC ACID, BY S. J. LLOYD**

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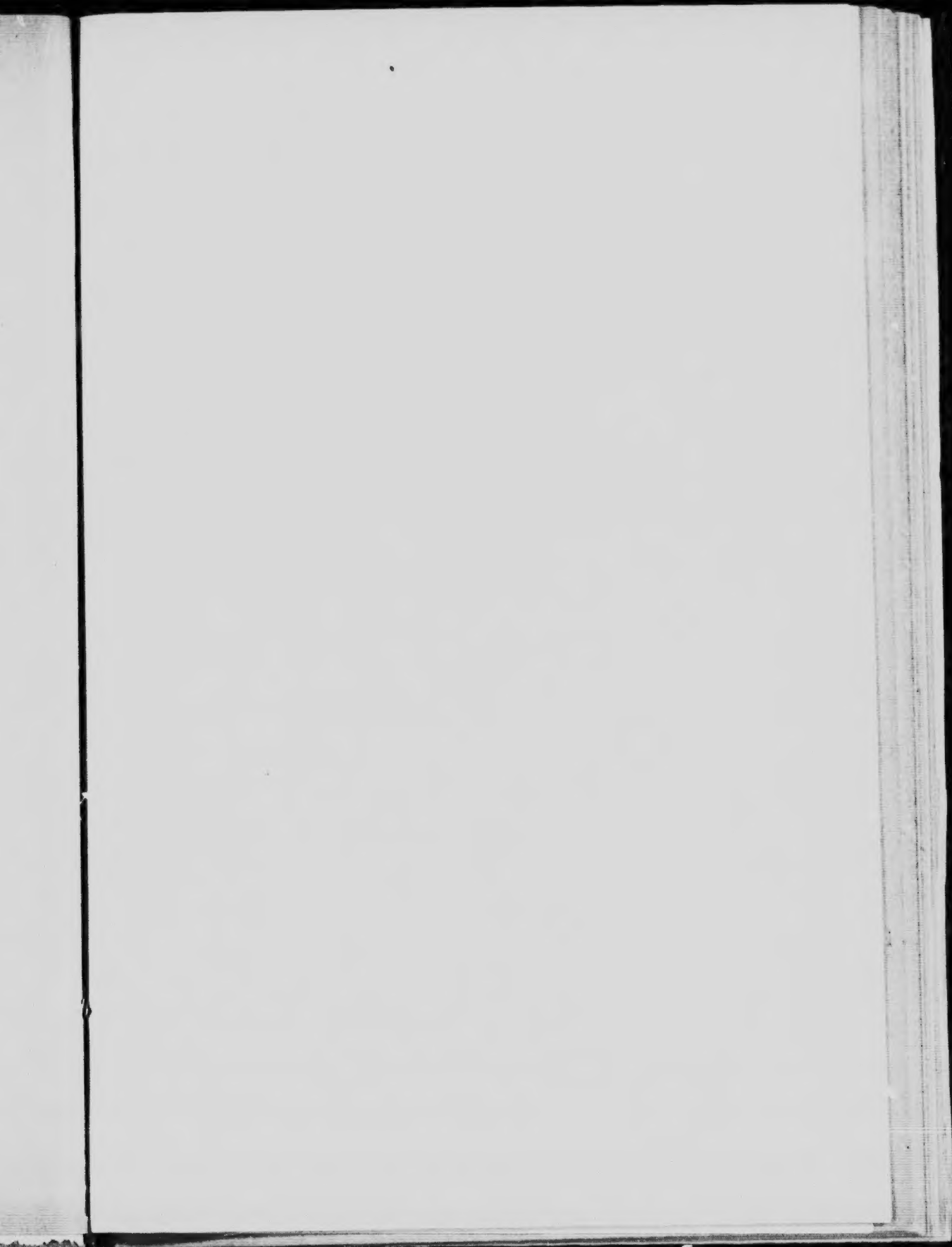
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THE DETERMINATION OF PHENOL.

BY S. J. LLOYD.

Received October 27, 1904.

NUMEROUS attempts have been made to devise a satisfactory method for the quantitative estimation of phenol.

Beckurts¹ mixed the phenol with its own volume of petroleum spirit, shook with a strong solution of caustic soda in a graduated tube, and noted the change in volume; Bader² titrated against a decinormal solution of sodium hydroxide with symmetrical tri-nitrobenzene as indicator;³ Messinger and Vortmann⁴ precipitated the triiodo derivative with an alkaline solution of iodine; Carre⁵ treated the phenol with nitric acid and determined the resulting picric acid colorimetrically; Schaedler⁶ used sulphuric acid, and determined the phenolsulphonic acid indirectly with barium; Riegler⁷ weighed the precipitate with *p*-diazonitraniline; Toscher⁸ oxidized with volumetric permanganate in boiling alkaline solution; while the reaction with sodamide has been applied by Schryver⁹ to the determination of the "hydroxyl value" of phenol.

Of these methods, the first evidently makes no pretense to accuracy, and indeed, like the sulphonic acid process, is intended for use with crude phenol only. Titration with soda is not possible with solutions containing less than 2 per cent. of phenol,¹⁰ and in any case the end-point is not sharp. Precipitation with iodine requires careful manipulation and exact regulation of the temperature in order to obtain accurate results;¹¹ the colorimetric method is unsuited to the determination of phenol in other than very small quantities, the reaction with the diazo compound leads to a tedious gravimetric process, and the sodamide method requires special apparatus, and can be used only with perfectly dry phenol.

The reaction of phenol, however, which is best suited for the

¹ *J. Soc. Chem. Ind.*, 5, 546 (1886) (from *Arch. Pharm.*, 24, 567 (1886)).

² *Ztschr. anal. Chem.*, 31, 58 (1892).

³ For the behavior of phenol with other indicators, see Imbert and Astruc: *Compt. Rend.*, 130, 35 (1900).

⁴ *Pharm. Zig.*, 29, 759.

⁵ *Compt. Rend.*, 113, 139 (1891).

⁶ *Centrbl.*, 1872, p. 506 (from *Pharm. Centrbl.*, 13, 225).

⁷ *Centrbl.*, 1899, II, p. 322 (from *Buletinul din Bucuresti*?).

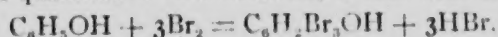
⁸ *Meyer's Jahrbuch, d. Chemie*, 1901, p. 253 (from *Pharm. J.*, 1901, No. 1602).

⁹ *J. Soc. Chem. Ind.*, 18, 553 (1899).

¹⁰ *Frerichs: Centrbl.*, 1896, II, p. 2141 (from *Apoth. Zig.*, 11, 415).

¹¹ *Frerichs: Loc. cit.*

purposes of quantitative determination, is that with bromine,



Landolt,¹ who was the first to suggest its use, precipitated the tribromophenol with bromine water, dried in a desiccator and weighed; Chabrie² extracted with ether and dried in a special apparatus. Koppeschaar³ shortened the process by using a measured quantity of bromine water, and titrating back the excess with potassium iodide and sodium thiosulphate; he also found it advisable to replace the unstable and disagreeable bromine water by a mixture of potassium bromide and bromate, from which the bromine was liberated at the proper time by acid. Degener,⁴ who was apparently unacquainted with Koppeschaar's work, also used bromine water, but determined the end-point by the disappearance of the yellow color of the solution, or by potassium-iodide-starch paper. Chandon⁵ found the time required for an analysis by the Koppeschaar method too long, and in order to shorten it and avoid loss of bromine as vapor and as a mechanical enclosure in the precipitate, he substituted for the bromide-bromate mixture a hypobromite solution which contained sufficient alkali to hold the tribromophenol in solution. The disappearance of the yellow color of the solution, or the failure to discolor potassium-iodide-starch paper, marked the end of the reaction. Waller⁶ used volumetric sodium hypochlorite, which he added to the solution of phenol containing excess of potassium bromide, and determined the end-point by the color of the solution. Waller's⁷ method differed from that of Degener only in the addition of a saturated solution of alum to make the precipitate more dense. Scherbert⁸ followed Koppeschaar in liberating the bromine from a bromide-bromate mixture, and added the phenol solution from a burette until the filtrate gave no further color with potassium-iodide-starch paper, while Beckurts⁹ used an excess of the bromine-bromide mixture, and titrated back with iodide and thiosulphate. The named chemist recognized the presence of tribromophenol.

¹ *Ber. d. chem. Ges.*, 4, 770 (1871).

² *Centrbl.*, 1898, 1, 1309 (from *Rev. Chim. Anal. Appl.*, 6, 138 (1898)).

³ *Ztschr. anal. Chem.*, 18, 233 (1876).

⁴ *J. prakt. Chem.*, N. F., 17, 390 (1878).

⁵ *Bull. Soc. Chim.*, 38, 69 (1882).

⁶ *Chem. News.*, 83, 51 (1901).

⁷ *Ibid.*, 43, 152 (1881).

⁸ *Ber. d. chem. Ges.*, 14, 1581 (1881), (from *Arch. Pharm.*, 18, 321).

⁹ *J. Soc. Chem. Ind.*, 5, 546 (1886) (from *Arch. Pharm.*, 24, 561 (1886)).

in the precipitate, but assumed that it was quantitatively converted into tribromphenol by potassium iodide

The following table may serve as a synopsis:

Gravimetric:

- (1) Landolt, Chablié.

Volumetric:

- (2) *Bromine and phenol in acid solution.*

- (a) End-point determined by color, or by potassium-iodide-starch paper.

Degener—Bromine water.

Telle —Hypochlorite and potassium bromide.

Waller —Bromine water and alum.

Seubert —Bromide-bromate mixture.

- (b) Excess bromine determined by potassium iodide.

Koppeschaar—Bromine water or bromide-bromate mixture.

Beckurts—Bromide-bromate mixture.

- (3) *Bromine and phenol in alkaline solution.*

Chandelon.

Various modifications for use in the estimation of phenol in tar-oil, urine, soaps, etc., have been suggested by Tóth,¹ Kleinert,² Fedeli,³ Giacosa,⁴ Endemann, Neuberg,⁵ Kossler and Penny,⁶ Partheil,⁷ Ditz and Cedivoda,⁸ Stockmeier and Thurnauer⁹ (who used chloroform in the titration), and others.

Some idea of the accuracy of the results obtainable by these different methods of procedure may be gleaned from the test analyses published by their authors. Landolt's numbers show variations of 0.5 per cent. or more. Koppeschaar's (bromine water) 2.5 per cent. (bromide-bromate) 0.5 per cent., Degener's 3 per cent., Chandelon 2 per cent., Seubert's 1.5 to 3 per cent. No test analyses have been published by Waller or Telle. According to Frerichs,¹⁰ Beckurt's modification is the best, but as his paper, in its original form, is not accessible to me, I am unable to quote the results of this author's analyses.

These discrepancies are due, in part at least, to the formation

¹ *Ztschr. anal. Chem.*, **25**, 160 (1886).

² *Ibid.*, **23**, 1 (1884).

³ *Ber. d. chem. Ges.*, **28**, 1060 R (1895), (from Moleschott's *Untersuchung.*, **18**, 583).

⁴ *Ztschr. physiol. Chem.*, **6**, 43 (1878).

⁵ *Ibid.*, **27**, 123 (1899).

⁶ *Ibid.*, **17**, 117 (1889).

⁷ *Meyer's Jahrbuch d. Chemie*, 1896, p. 237 (from *Apoth. Ztg.*, 1896).

⁸ *Ztschr. angew. Chem.*, 1899, pp. 873 and 897.

⁹ Mohr: *Titrimethode*, 7th ed., p. 386 (1896) from *Chem. Ztg.*, 1893, pp. 1 and 12.

¹⁰ *Centrbl.*, 1896 (II), 2141.

of tribromophenolbromide, which, as I have shown in a previous paper,¹ is produced by the action of bromine water on the precipitated tribromophenol, and once formed is not quantitatively reconverted into tribromophenol by potassium iodide.

The present paper, after dealing with the loss of bromine by evaporation during the analysis, the use of volumetric solutions containing bromates, and the formation of a new product of the action of bromine on phenol, contains the results of a number of test-analyses in which the precautions suggested by the previous experiments were adopted, and closes with an enumeration of the conditions under which phenol may be accurately determined.

SOLUTIONS EMPLOYED.

Phenol.—Merck's "absolute phenol" was distilled three times, the first and last fractions being rejected in each case, and the portions boiling between 182° and 183° collected. In the last fractionation the distillate was received in a tared and stoppered weighing-glass, cooled, weighed (20.5340 grams) and dissolved to 1 liter. The solution used in the following analyses was made by diluting 100 cc. of this solution to 1 liter.

Hypobromite.—About 9 cc. of bromine were dissolved in 2 liters of N/4 caustic potash, and the solution was standardized by adding potassium iodide and hydrochloric acid, and determining the iodine with decinormal thiosulphate.

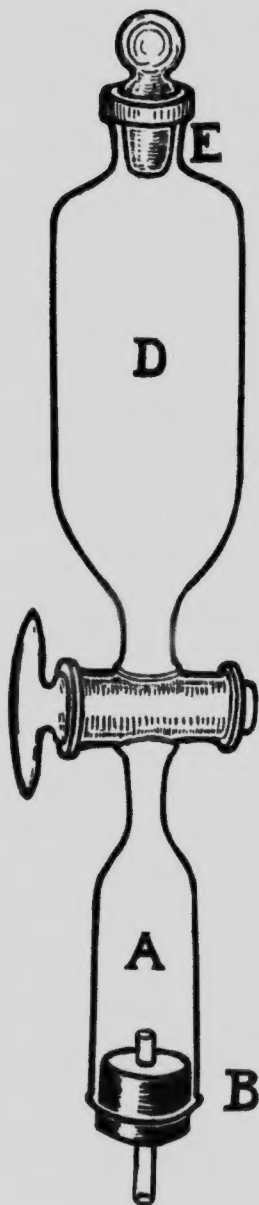
One hundred cc. of the phenol solution were equivalent to 71.95 cc. of the hypobromite.

Sodium Thiosulphate.—One liter of an approximately N/10 solution was prepared and standardized with iodine which had been ground with potassium iodide, sublimed from the mixture, and dried for three days in a vacuum desiccator over sulphuric acid. The value was found to be 0.1045 N. This solution was used to fix the titre of the alkaline solution of bromine as stated above, and in turn was repeatedly standardized against the latter solution; it showed a slight falling off in normality from 0.1045 to 0.1042 in two weeks.

For use in the phenol determination the decinormal thiosulphate was diluted to five times its volume and the ratio controlled by comparison with an iodine solution.

Iodine, approximately N/50 for use in "titrating back."

¹ This Journal, 27, 7 (1905).



poured through *E* into a beaker containing 150 cc. of water, where

Acid, hydrochloric, "strictly chemically pure" (sp. gr. 1.2).

Potassium Iodide, 17 grams in 100 cc.

The solutions were prepared and standardized with every care, the burettes were calibrated before using, and a special burette reader was employed, by means of which hundredths of a cubic centimeter could readily be distinguished.

LOSS OF BROMINE BY EVAPORATION.

The test analyses published at the close of this paper were carried out in a 0.25 liter long-necked glass-stoppered measuring flask. In order to assure myself that there was no loss of bromine by evaporation, two measurements were made in the apparatus sketched in the accompanying figure (made by sealing an adapter to a separating funnel).

The chamber *A* was closed by the perforated rubber stopper *B*, the tap opened and the whole exhausted with a filter-pump; the tap was then closed, *B* removed, and the apparatus fixed in a stand, *A* upwards. Fourteen cc. of the hypobromite (or bromide-bromate solution) were then pipetted into *A* and sucked into *D* by slightly opening the tap; this was followed by 25 cc. of acid and then 20 cc. of phenol solution; the vessel *A* was rinsed out with 10 cc. of water between each addition and the rinsings sucked into *D*. After shaking and allowing to stand for five minutes, 5 cc. of the potassium iodide solution were added in the same manner; the tap was then opened to restore atmospheric pressure in *D* and the contents

the iodine was titrated by sodium thiosulphate. From the thiosulphate required the excess of bromine was calculated, and by subtracting from the original 14 cc. the "KBr used" of the table was obtained.

Experiments identical in every respect, except that the 250 cc. flask was used instead of the apparatus just described, were carried out at the same time; as is shown in Table I, the results differ only by one or two parts per thousand. It is thus proved that the operation may be carried out in a flask without loss of bromine. Some care, however, is necessary; in one case where the bromine vapor was purposely blown out of the flask, an error of 2 per cent. in the analysis resulted.

TABLE I.

Hypobromite, 14 cc.; acid, 25 cc.; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Apparatus.	KBr used.	Differences.
Fresh	Flask	13.91	0.0
Fresh	See figure	13.91	
Evaporated	Flask	13.96	0.02
Evaporated	See figure	13.94	

ACTION OF BROMIC ACID ON PHENOL AND THE USE OF THE BROMIDE-BROMATE MIXTURE.

If a little potassium bromate be mixed with a solution of phenol and acid be added, the solution turns red and a red precipitate is deposited which contains bromine and does not liberate iodine with hydriodic acid. It is obvious that the formation of this substance, during the determination of phenol, would vitiate the result.

As old solutions of potassium hypobromite are liable to contain bromate, two pairs of experiments were undertaken to see whether errors could be introduced into the analysis from this source; in one of each pair 14 cc. of fresh hypobromite solution were used and in the other a solution of bromide and bromate made by evaporating 14 cc. of the same hypobromite to dryness and dissolving the residue. In one experiment of each of the pairs the reagents were mixed in the order *A*, hypobromite (or bromide-bromate mixture), acid, phenol, and in the other in the order *B*, acid, phenol, hypobromite (or bromide-bromate). The results with the bromide-bromate mixture were 3 or 4 parts per thousand higher than the others, while the order of mixing made no difference (see Table II). It is thus clear that the presence of a little bromate

in the hypobromite solution can exert no influence whatever on the result.

TABLE II.

Hypobromite, 14 cc. ; acid, 25 cc. ; water, 30 cc. ; phenol, 20 cc. ; iodide, 5 cc. ; time, five minutes.

Hypobromite.	Order of mixing.	KOBr used.
Fresh	<i>A</i>	13.91
Fresh	<i>B</i>	13.94
Evaporated	<i>A</i>	13.96
Evaporated	<i>B</i>	13.96

NEW PRODUCT OF THE ACTION OF BROMINE ON PHENOL.

If solutions of phenol and potassium hypobromite be mixed and the mixture be acidified, the precipitated tribromphenol is mixed with a red powder. What seems to be the same compound was obtained as a by-product in the preparation of tribromphenolbromide, and by the action of alkaline solutions of bromine on tribromphenol. It melts at about 91° C. and contains about 64 per cent. of bromine, but does not liberate iodine with an acid solution of potassium iodide. It is insoluble in water, alcohol, ether, and in glacial acetic acid; soluble in carbon bisulphide, chloroform and benzene, giving red solutions. Its molecular weight in chloroform solution (boiling-point determinations) is 508 to 514. On warming with a 10 per cent solution of caustic potash, or with concentrated sulphuric acid, it is apparently unaltered, but by heating to a temperature above its melting-point it is converted into a substance resembling hexabromophenoquinone.

I propose, if possible, to determine the constitution of this substance. Its formation during an analysis would, obviously, introduce errors into the result, hence the analytical method of group 3 (page 18) cannot be recommended.

THE DETERMINATION OF PHENOL.

Four of the most likely sources of error in the present methods of determining phenol by bromine having been studied in detail, it remained to inquire whether determinations carried out under the conditions suggested by the foregoing experiments, would give accurate results. The test-analyses undertaken with the object of deciding this question were made in acid solution in order to avoid the formation of tribromphenolbromide;¹ they were carried out at room temperature in a long-necked, glass-stoppered 0.25-liter flask (page 20), and the bromine was introduced in the convenient form of a solution in caustic potash (page 22). The

¹ This Journal, 27, 7 (1905).

phenol solution was run into the flask from a burette, the acid added, and then the hypobromite from a pipette. The flask was closed, shaken for thirty seconds, and allowed to stand for the time given in the table after "t." Five cc. of potassium iodide solution were then added, followed by 100 cc. of water, and in some cases 10 cc. of chloroform. The whole was shaken for fifteen seconds, allowed to stand for two minutes, and the iodine determined with the N/50 thiosulphate.

TABLE III.
Hypobromite, 25 cc.; acid, 15 cc.
10 cc. chloroform. No chloroform.

Phenol. cc.	Excess Br. cc.	10 cc. chloroform.		No chloroform.		
		<i>t</i> = 0. Per cent.	<i>t</i> = 2 min. utes. Per cent.	<i>t</i> = 0. Per cent.	<i>t</i> = 2 min. utes. Per cent.	<i>t</i> = 5 min. utes. Per cent.
5	21.40		114.0	105.6	105.6	106.2
10	17.80		109.6	103.9	103.7	103.9
15	14.21		100.10			
20	10.61	100.0	99.95		99.97	100.11
20	10.61				101.51*	102.71†
20	10.61					101.92†
25	7.01		100.05	99.62	99.83	99.83
25	7.01				100.35†	
25	7.01				99.85	
30	3.42	99.9	99.95	99.56	97.7	99.83
30	3.42			99.6	99.65	99.85
31	2.70	99.8	99.8	99.44	99.55	99.97
32	1.98		99.85	99.25	99.35	99.97
33	1.26		98.99	98.7	99.35	99.7
34	0.54		98.62	98.1	98.9	99.42
35	0.18		97.63	96.9		98.74

Under "Excess Br" is given the difference between the volume of the hypobromite employed, *viz.*, 25 cc. and the volume equivalent to the phenol taken (volume of phenol solution multiplied by 0.7195, see page 19). The results of the determinations are expressed as percentages of the amount of phenol actually present.

In the experiments marked with a star (*), 10 cc. of carbon bisulphide were used instead of chloroform, and in that marked dagger (†), 5 cc. of acid were used instead of 15 cc. In this experiment the precipitate, dissolved in chloroform, gave a distinct green with benziné solution, indicating the presence of tribromophenolbromide.

Table IV contains the results of a few measurements in which sulphuric acid was used instead of hydrochloric. It is obvious that Koppeschaar¹ was mistaken in saying that the presence of sulphuric acid spoils the titration.

¹ *Ztschr. anal. Chem.*, 18, 237 and 240.

TABLE IV.

Hypobromite, 25 cc.; sulphuric acid (sp. gr. 1.84), 11 cc.; chloroform, 10 cc.

Phenol. cc.	Excess Br. cc.	$t = 2$. Per cent.
20	10.61	99.91
25	7.01	99.85
30	3.42	100.11

The above experiments lead to the following:

DIRECTIONS FOR THE DETERMINATION OF PHENOL BY BROMINE.

The following solutions are needed.—Fiftieth-normal thiosulphate and iodine; starch; hydrochloric acid (sp. gr. 1.2); potassium iodide, 17 grams in 100 cc.; hypobromite, prepared by dissolving 9 cc. of bromine in 2 liters of a solution containing 28 grams of caustic potash. The hypobromite must be compared with the thio-sulphate by adding acid and potassium iodide and titrating the iodine set free.

To carry out the analysis.—Introduce the phenol solution into a glass-stoppered flask and add a volume of acid equal to about one-third or one-fourth of the combined volumes of the phenol solution and the hypobromite that will probably be added during the analysis.

Run in the hypobromite from a burette, shaking the flask, until the solution becomes permanently yellow. Then add an excess of the hypobromite (10 to 20 per cent. of that used already) and shake well. Finally add an excess of potassium iodide, dilute with water, add 10 cc. of chloroform, and determine the iodine with the volumetric thiosulphate. The object of diluting is to prevent the acid from acting on the potassium iodide or on the thiosulphate; if 10 cc. of water be added at this stage for every cubic centimeter of acid previously added, the solution will be sufficiently dilute. The use of chloroform may be dispensed with, if the mixture be allowed to stand five minutes before adding the potassium iodide; it is, however, better to use the chloroform,—carbon bisulphide is not satisfactory.

If these directions be adhered to, the phenol can be determined within 1 or 2 parts per thousand.

In conclusion, the author wishes to express his thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

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March, 1904.

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TRIBROMPHENOLBROMIDE: ITS DETECTION, ESTIMATION, RATE OF FORMATION, AND REACTION WITH HYDRIODIC ACID.

By S. J. LLOYD.

Received October 27, 1904.

THE following experiments form part of an investigation of the reaction between bromine and phenol, which was undertaken with the object of improving Koppeschaar's method of determining the latter substance.

The tribromphenolbromide used was prepared by Werner's¹ recipe, recrystallized three times from chloroform, and dried for three days over sulphuric acid in a vacuum; it formed golden-yellow crystals, melting-point 119° .

DETECTION.

When searching for a distinctive qualitative test for tribromphenolbromide, I found that ammonia, and chloroform solutions of many of the organic bases react with it to form colored products, as follows:

¹*Bull. Soc. Chim.*, **43**, 372 (1885)

Ammonia	Brown.
Aniline	Deep red, turning muddy.
Dimethylaniline	Slight darkening.
Paratoluidine	Clear red
Diphenylamine	Light red.
α -Naphthylamine	Dark blue, turning purple.
β -Naphthylamine	Light rose-pink, appears very slowly.
Aminoazobenzene	Brown-red, appears very slowly and gradually deepens.
Pyridine	Light yellow.
Benzidine	Intense green, purple if concentrated.
Azoxybenzene, Metanitriline, Acetanilide,	no change.

Of these, aniline and benzidine proved most suitable as reagents; with tribromphenol, tetrabromphenol and hexabromphenoquinone they give no color, while with bromine water an aniline solution is bleached, and benzidine gives a seal-brown, quite distinct from the green with tribromphenolbromide.

The benzidine solution may be prepared by warming 5 grams of benzidine sulphate with 50 cc. of a 10 per cent. potash solution, cooling, extracting the benzidine with chloroform, and filtering off the chloroform solution. Three drops of this reagent give a distinct green with 10 cc. of a solution containing 1 gram of tribromphenolbromide in a liter of chloroform. Shaking the tribromphenolbromide solution with decinormal sodium thio-sulphate before adding the benzidine reagent does not interfere with the color reaction.

ESTIMATION.

As the reaction with potassium iodide is obviously unsuitable (see page 20), a basis for the method was sought in the action of reducing agents; Benedict¹ states that zinc and hydrochloric acid reduce tribromphenolbromide to tribromphenol, but does not seem to have made any quantitative measurements. After experimenting with sodium amalgam and with magnesium, I finally decided in favor of powdered zinc and sulphuric acid, which are without action upon tribromphenol, but remove one atom of bromine from tribromphenolbromide. By determining the bromine in the solution after reduction, it is thus possible to calculate the amount of tribromphenolbromide in the substance analyzed. The details of the method are as follows:

The tribromphenolbromide was placed in a 150 cc. flask, 20 cc.

¹ *Ann. Chem. (Liebig)*, 199, 127 (1879).

of alcohol (96 per cent.), 5 cc. N/4 sulphuric acid and about 0.25 gram powdered zinc¹ were added, and the flask heated on a water-bath until the whole of the tribromphenolbromide had dissolved and the solution had lost its characteristic yellow color. Excess of calcium carbonate was then added to neutralize the free sulphuric acid, and the alcohol together with most of the tribromphenol were distilled off on a water-bath; the residue was extracted with three successive portions of boiling water, 25 cc., 25 cc., and 10 cc., respectively; and in the filtrate, after cooling, the bromine was determined by N/10 silver nitrate with potassium chromate as indicator. Blank experiments with tribromphenol showed that no bromine was removed by this treatment.

TEST ANALYSES.

Tribromphenol- bromide. Gram.	AgNO ₃ found. cc.	AgNO ₃ calc. cc.	Per cent
0.5023	12.45	12.46	99.92
0.5327	13.19	13.11	100.61
0.5249	12.80	12.92	99.07

NOT THE PRIMARY PRODUCT.

The precipitate formed by the action of bromine water upon phenol is at first pure white in color, but on standing with the solution containing excess of bromine it gradually assumes a yellowish tint; the change is due to the formation of tribromphenolbromide, the presence of which was detected by the qualitative tests described above. The change of color shows that tribromphenolbromide is not the primary product of the action of bromine water upon phenol, as imagined by Weinreb and Bondi,² but is formed by a gradual reaction between the precipitated tribromphenol and the excess of bromine.

RATE OF FORMATION.

By means of the method of analysis described above, the amount of tribromphenolbromide formed when the phenol was treated with bromine under varying conditions was determined.

The following solutions were employed: *Phenol*, 20 grams per liter; *silver nitrate*, 16.83 grams per liter; the tribromphenolbromide from 5 cc. of the phenol solution is thus equivalent to 10.74 cc. of the silver nitrate. *Hypobromite*, bromine was dissolved in a solu-

¹ This is more than enough, excess does no harm.

² *Monatsh. Chem.*, 6, 506 (1885).

tion of caustic potash of known alkalinity (about quarter normal) and a solution of *hydrochloric acid* equivalent to the potash was prepared, so that on mixing the alkaline solution of bromine with an equal volume of the equivalent acid a neutral bromine solution resulted. By titration with volumetric sodium thiosulphate after adding acid and potassium iodide, 50 cc. of the hypobromite solution were found to contain 0.6810 gram bromine; hence to convert 5 cc. of the phenol solution into tribromophenol requires 37.45 cc. of the hypobromite solution; to convert it into tribromophenolbromide requires 49.94 cc. Allen¹ states that hypobromite solutions prepared like that above, and containing a large excess of alkali do not appreciably alter their content of available bromine upon standing or heating.

The experiments were carried out as follows: 50 cc. of the hypobromite solution were pipetted into a glass-stoppered quarter-liter measuring flask, then 50 cc. of the equivalent acid added and finally 5 cc. of the phenol solution. The mixture was shaken for thirty seconds and allowed to stand for a measured interval, after which the mother-liquor was rapidly removed by means of a filter-pump and a large perforated porcelain funnel. The precipitate was washed with cold water until the addition of silver nitrate produced no cloudiness in the filtrate, and was then brought, filter-paper and all, into a 150 cc. flask, where the tribromophenolbromide was determined as described above.

In some of the experiments the concentration of the bromine was altered by adding bromine from a burette; in others, previous to the addition of phenol, the solution was acidified with hydrochloric acid (sp. gr. 1.2), while in others weighed quantities of potassium bromide were added. The results are contained in Tables I to VI.

The effect of varying the time during which the bromine water acted upon the tribromophenol, *i. e.*, the interval between adding the phenol and filtering, was first studied. The results of these experiments are contained in Table I; they afford ample proof that the tribromophenolbromide is a secondary product and show what a large amount of it may be formed in a few minutes under the ordinary conditions of a phenol determination.

¹ *J. Soc. Chem. Ind.*, 3, 65 (1884).

TABLE I.—EFFECT OF TIME.

KBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Time. Minutes.	AgNO ₃ cc.	Tribromphenolbromide. Per cent.
5	2.36	22
10	4.11	38
15	5.13	48
30	7.49	70
Hours. 18	7.75	72

Under AgNO₃ is given the volume of the silver nitrate solution required in the analysis; the numbers under "Tribromphenolbromide" (obtained by dividing the figures in the second column by 10.74) represent the fraction of the phenol which has been converted into tribromphenolbromide.

The experiments of Tables II, III, IV, V and VI show that the amount of tribromphenolbromide formed from 5 cc. of the phenol solution in a constant interval (five minutes) increases with the excess of bromine and with the volume of the reacting mixture, and is diminished by adding acid or potassium bromide, or by lowering the temperature. They afford a striking parallel to the results obtained by Mr. Roebuck in his study of the rate of oxidation of arsenious acid by iodine,¹ where the rate is proportional to the concentration of the iodine and to the volume of the solution, and inversely proportional to the concentration of the acid and of the potassium iodide; Roebuck interpreted his results by assuming that hypiodous acid is the oxidizing agent in iodine solutions; a similar explanation of my own experiments, viz., that the formation of tribromphenolbromide from tribromphenol is due to the oxidizing action of hypobromous acid, naturally suggests itself.

TABLE II.—EFFECT OF VOLUME.

KBr, 50 cc.; equiv. HCl, none; * HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Volume. cc.	AgNO ₃ cc.	Tribromphenolbromide. Per cent.
57	1.19	11
106	2.36	22
157	3.84	36
207	4.6	43

* To keep down the volume. The 1 cc. of strong hydrochloric acid was very slightly more than enough to neutralize the alkali of the hypobromite solution.

¹ *J. Phys. Chem.*, 6, 365 (1902).

TABLE III.—EFFECT OF BROMINE.

KBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total excess bromine. Grams.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0.17	2.36	22
0.55	5.59	52
0.92	7.02	66
1.67	8.74	81

TABLE IV.—EFFECT OF ACID.

KBr, 50 cc.; equiv. HCl, 50 cc.; phenol, 5 cc.

Total acid. Mol.	AgNO ₃ . cc.	Trioromphenolbromide. Per cent.
0.016	2.36	22
0.029	2.78	17
0.068	1.37	13
0.068	1.35	13
0.133	0.35	3
0.198	0.1	1

TABLE V.—EFFECT OF POTASSIUM BROMIDE.

KBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total KBr. Mol.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0.003	2.36	22
0.0073	1.69	15.7
0.0116	0.51	4.7
0.0288	0.25	2.3
0.0546	0.23	2.2

TABLE VI.—EFFECT OF TEMPERATURE.

KBr, 50 cc.; equiv. HCl, 50 cc., HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

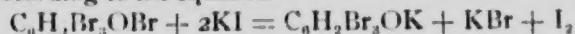
Temperature. °C.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0	1.9	18
18	2.36	22

These experiments show clearly that in order to avoid the formation of tribromphenolbromide when titrating phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide; the excess of bromine must not be too great, and the time during which the precipitate of tribromphenol is in contact with the excess of bromine must not be too long. Under these conditions only a mere trace of tribromphenolbromide is formed, and it is precisely when the quantity of that substance is smallest that it is most easily acted upon by hydriodic acid (see Table VII).

TRIBROMPHENOLBROMIDE.

REACTION WITH HYDRIODIC ACID.

The statement that tribromphenolbromide reacts with potassium iodide according to the equation



is founded on experiments of Weinreb and Bondi,¹ and of Werner.² The former obtained 95 per cent. of the theoretical iodine by digesting for twelve hours with an aqueous solution of potassium iodide at 18°, or 99 per cent. at 50°; the latter, using a chloroform solution, obtained 99.96 per cent. The more recent experiments of Kastle,³ however, show that in chloroform solution, in absence of water, hexabromphenoquinone is the sole product, in which case only half of the iodine called for by the above equation is liberated, while if a carbon bisulphide solution of tribromphenolbromide be treated with an aqueous solution of potassium iodide, the iodine liberated varies from 90 to 100 per cent. of the theoretical amount, depending upon the relative quantities of potassium iodide, water, and carbon bisulphide present. In none of my own experiments, the results of which are detailed in Tables VII and VIII, did I obtain a quantitative yield of iodine; although potassium iodide was present in excess, the acidity of the solution was varied, different solvents were tried, and the digestion was much more prolonged than would be convenient in an analytical method.

It is apparent, however, that as the amount of tribromphenolbromide is reduced, the amount of iodine liberated approaches nearer and nearer to the theoretical value.

TABLE VII.

Expt.	Tribrom-phenol-bromide. Gram.	Solvent.	Time.	n HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
i	0.2038	none	7 days	..	77	
ii	0.2031	"	7 days	..	78	
iii	0.1747	CHCl ₃	24 hrs.	..	87	Brown, not green with benzidine.
iv	0.1560	CHCl ₃	20 hrs.	2.5	91	Deep red with aniline
v	0.1775	CHCl ₃	8 hrs.	2.5	88	Yellowish red; not green with benzidine.
vi	0.2520	C ₆ H ₆	48 hrs.	..	76	Deep red with aniline.
vii	0.2685	C ₆ H ₆	36 hrs.	5	81	" " " "
viii	0.3045	C ₆ H ₆	24 hrs.	5	84	" " " "
ix	0.2073	C ₆ H ₆	10 min.	5	78	Green with benzidine.

¹ *Monatsh. f. Chem.*, **6**, 506 (1885).

² *Bull. Soc. Chim.*, **43**, 373 (1885).

³ *Am. Chem. J.*, **27**, 31 (1902).

Expt.	Tribrom- phenol- bromide. Gram.	Solvent.	Time.	N HCl cc.	Iodine. Per cent.	Chloroform or benzene residues.
<i>x</i>	0.2594	C_6H_6	1 hr.	5	80	Green with benzidine.
<i>xi</i>	0.0017	$CHCl_3$	5 min.	5	98	Too dilute.
<i>xii</i>	0.0034	$CHCl_3$	5 min.	5	94	" "
<i>xiii</i>	0.0068	$CHCl_3$	5 min.	5	91	" "
<i>xiv</i>	0.0102	$CHCl_3$	5 min.	5	87	" "
<i>xv</i>	0.0170	$CHCl_3$	5 min.	5	83	" "

In Experiments *i* to *x* the amount taken for analysis was weighed out and placed in a 100 cc. glass-stoppered bottle, the benzene or chloroform (10 cc.) added, then the acid and finally the potassium iodide dissolved in water. In Experiment *v* four times the theoretical amount of potassium iodide was used, in the others twice. The mixture was well shaken and allowed to stand for a measured time, at the end of which the iodine set free was titrated against N/50 thiosulphate. The results of the analyses are entered in the table under "Iodine" as percentages of the amounts of iodine that would have been liberated from the tribromphenolbromide taken had the reaction proceeded according to Werner's equation.

In Experiments *xi* to *xv* a weighed quantity of tribromphenolbromide was dissolved in chloroform, and a measured volume of this solution made up to 10 cc. for each experiment, 5 cc. of normal potassium iodide and 5 cc. of normal acid were added, and the mixture was well shaken and allowed to stand for five minutes, after which the iodine was determined as before.

After completing the analysis, the color of the chloroform or benzene solution was noted, and then a few drops of the aniline or benzidine reagent added. In Experiments *iv*, and *vi* to *x*, the presence of unaltered tribromphenolbromide was established, but in Experiments *iii* and *v*, although the chloroform solutions were colored, no tribromphenolbromide could be detected. This shows that in the experiments in question the deficit of 15 per cent. or so in the iodine is due to the formation of a by-product, and not to the incompleteness of the reaction formulated above. The delicacy of the benzidine test is not sufficient to enable it to be of value in Experiments *xi* to *xv*.

The experiments of Table VIII were carried out in the same way as the first ten of the preceding table, except that the hydrochloric acid was replaced by acetic, and an excess of sodium thiosulphate (5 cc. of a normal solution) was added to the reacting

mixture at the same time as the potassium iodide. The results are very similar to those of Table VI* show that the deficit is not altogether due to the presence of benzidine.

TABLE III.

No.	Tribrom-phenol-bromide, Gram.	Solvent.	Time, Hours.	HAc, cc.	Iodine, Per cent.	Chloroform or benzene residues
1	0.3195	C_6H_6	24	5	87	No reaction with benzidine.
2	0.1470	C_6H_6	20	5	95.8	" " " "
3	0.1795	C_6H_6	18	5	95.6	" " " "
4	0.2145	C_6H_6	24	5	92.1	" " " "
5	0.2748	$CHCl_3$	24	5	93.3	" " " "

From these experiments it is apparent that if in a phenol determination part of the tribromphenol precipitate is converted into tribromphenolbromide, the latter will not be quantitatively transformed into tribromphenol by the action of potassium iodide, and an error will thus be introduced into the analysis.

SUMMARY.

(1) Aniline and benzidine may be used as qualitative reagents for tribromphenolbromide.

(2) Tribromphenolbromide is quantitatively reduced to tribromphenol by zinc and sulphuric acid; a convenient method for its determination, based on this reaction, is described.

(3) Tribromphenolbromide is not a primary product of the action of bromine on phenol, but is formed by the gradual action of bromine water on tribromphenol. As the rate of this reaction is decreased by adding acid or potassium bromide, and increased by adding water or bromine (or by raising the temperature), it is probably due to the presence of hypobromous acid in the bromine water.

(4) Tribromphenolbromide is not quantitatively reduced to tribromphenol by hydriodic acid under conditions convenient for analysis; this is due in part to the formation of other products.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken and under whose supervision it has been carried out.

